Diffusion in Multicomponent Solids
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Lecture 32
Diffusion Mechanisms in Intermetallics

Welcome to the 32nd lecture of this open course on Diffusion in Multicomponent Solids. In this lecture I have discussed various Diffusion Mechanisms that have been proposed in intermetallics. I have illustrated these diffusion mechanisms with respect to B_2 structures. Last lecture, we went over the point defects in ordered structures, including ionic compounds and intermetallics.

Intermetallics is fast emerging as a new class of material especially for high temperature applications. Because they sustain very high temperatures and the study of diffusion in intermetallics has become very important. In this class we will go over some of the diffusion mechanisms that have been proposed in intermetallics.

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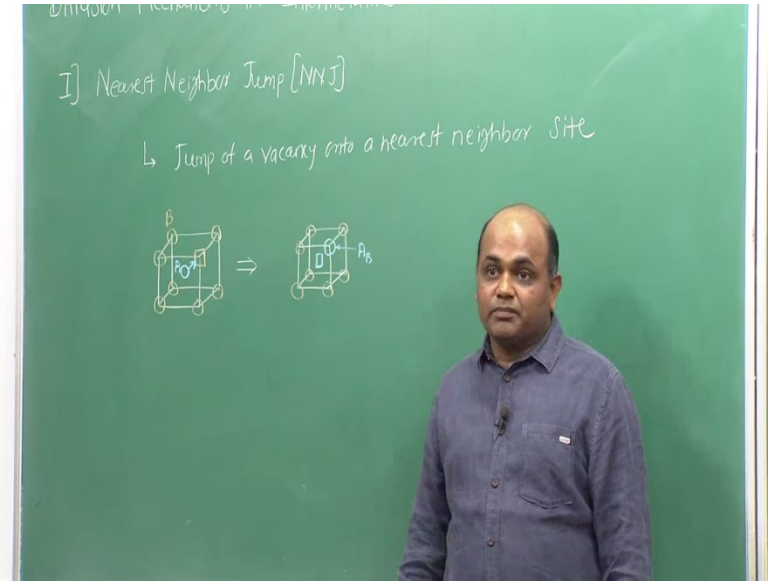

The first mechanism is called Nearest Neighbour Jump or in short NNJ. As the name suggests, it is simply a jump on to a nearest neighbour site and this is assisted by a vacancy or the jump of a vacancy on to a nearest neighbour site. Now, we consider a B_2 structure which has corner B

atoms shown by red colour and body centre A atoms denoted by blue colour. If there is a vacancy on a B sub lattice denoted by a square and since all the nearest neighbour in B_2 structure are different type, a different type of atom would jump into this vacancy by NNJ mechanism.

Type A atom can jump on to this nearest neighbour vacancy. This will lead to formation of an antisite of A. Once this jump occurs the vacancy has been moved to the A sub lattice and one A atom has been moved to a B sub lattice. So, this forms an antisite of A on B and you can imagine the NNJ mechanism would be operative if the formation of an antisite is a low energy event.

For example in nickel aluminide, especially on the nickel rich side, the nickel antisite equilibrium concentration is considerable and the nickel can diffuse by nearest neighbour jumps, but not for aluminium as aluminium antisite is a high energy structure. How does aluminium diffuse? It can diffuse by jump to a next nearest neighbour site.

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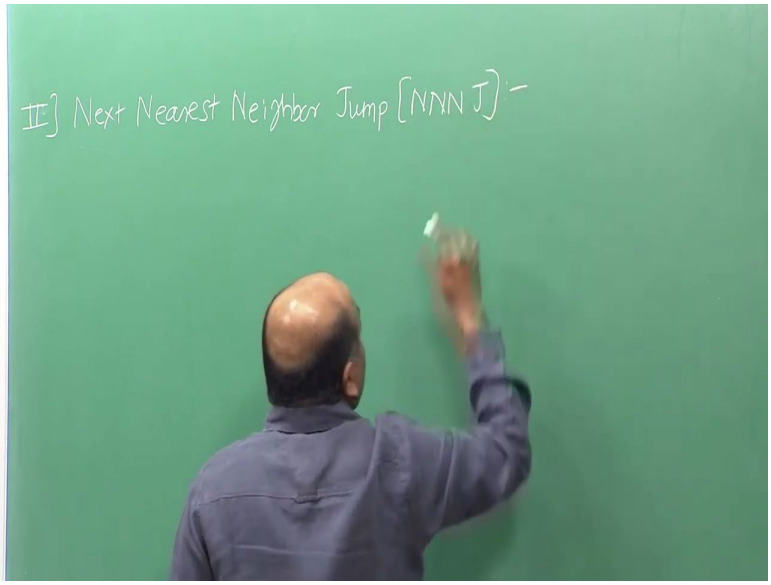

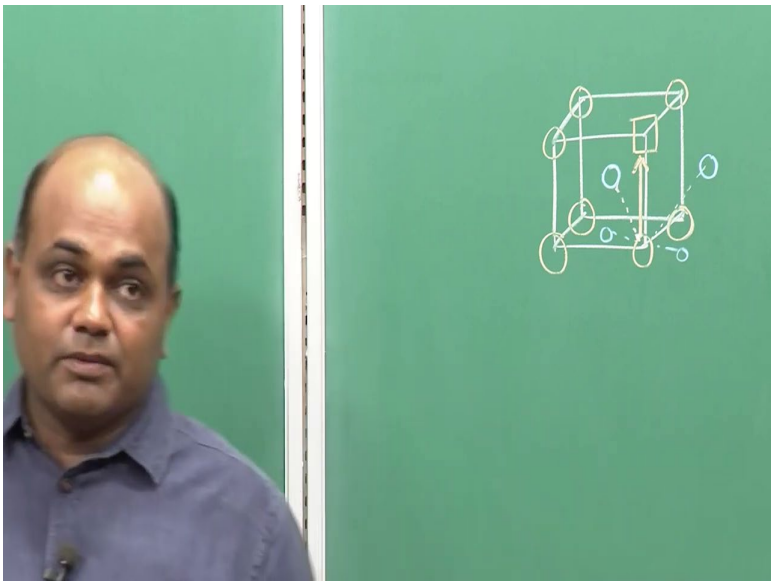

The second mechanism is Next Nearest Neighbour Jump or in short denoted as NNNJ. In a B_2 structure, if there is a vacancy on B sub lattice denoted by this square here and B atom is located only on to the next nearest neighbour site of this vacancy. So, another B atom can jump on to that vacancy and this is the next nearest neighbour jump. You can see exchanging with the vacancy on the next nearest neighbour site is not causing any disorder. That is, no wrong bonds are formed. However, this requires large activation energy, as each corner atom is touching the central atom. For example this B atom is bonded with four body centre A atoms denoted by blue colour and as this B atom is moving, it has to push apart these four A atoms and so, the activation barrier for the next nearest neighbour jump NNNJ is very high.

The NNNJ will be active if the ordering energy is very high. Because ordering energy is very high nearest neighbour will not be possible. Because the nearest neighbour jump will produce wrong bonds or disorder which will lead to a very high energy configuration. A nearest neighbour jump will be possible if the ordering energy is low or if one of the atom is very small. If the atom is very small than it can form an antisite and it can diffuse by nearest neighbour jump or NNJ whereas the larger atom will diffuse by NNNJ or next nearest neighbour jump.

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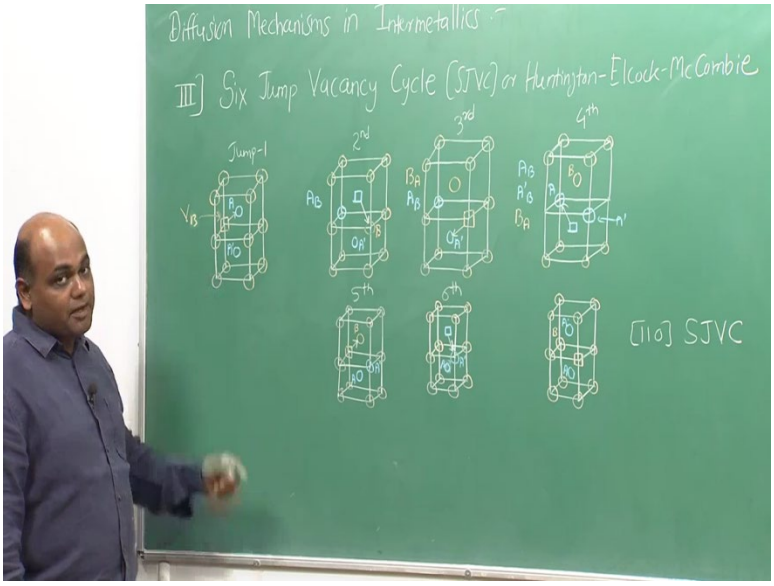

In ordered structure, especially in B_2 compounds we have seen the nearest neighbour jump leads to a disorder or formation of wrong bonds. However, if we consider sequence of jumps of a vacancy, at the end of which if the order is restored, that can be taken as unit step of diffusion. Since the order is restored at the end of this sequence of co-related jumps of the vacancy, the total energy or the total activation barrier for this type of mechanism can still be less than the next nearest neighbour jump barrier and this mechanism can be operative in ordered structure.

One such mechanism which was proposed is called a Six Jump Vacancy Cycle or after those who proposed this is also called as Huntington, Elcock, McCombie mechanism. As the name suggests, it consists of sequence of six jumps of a vacancy. Let me illustrate the SJVC mechanism in a B_2 crystal structure. I have shown two B_2 unit cubes here, one on top of the other. You can see 2 A atoms at the body centres of the cube. Let us denote this one by A and this is A' and there is a vacancy on the B sub lattice V_B. In the sequence of six jumps of the vacancy, all jumps are NNJ or nearest neighbour jumps. So, the first jump of the vacancy can be on this site A. This is jump 1. After that A will occupy a B sub lattice site. So, there is an antisite of A on B which is produced and the vacancy has moved to A sub lattice. Let us call this atom as B, because this will take part in this SJVC cycle and A' is still where it was. The next jump of the vacancy will be obviously on to a B sub lattice. let us say it exchanges with this atom B, as the B now jumps on to A sub lattice. There is one more antisite formed which is B on A.

We have B on A and there is A on B which was formed after the pervious jump. This was the second jump. A' is where it was and the vacancy has moved to a B sub lattice. The third jump of the vacancy will be with an A atom, let us say it exchanges with A' here, during the third jump. Now A' has also moved to B sub lattice. We have now, 3 antisites. A on B, A'on B, and then B on A and the vacancy is now in the position of A'.

Three antisites are now formed. The fourth jump of the vacancy will be most probably with an antisite A, this is the fourth jump. After the fourth jump A has restored its sub lattice. Of course A has switched its position on the A sub lattice and the vacancy has moved to B sub lattice. There are still two antisites left, B on A and A prime on B. During its fifth jump, the vacancy will now exchange with the antisite of B on A. The vacancy has now moved to an A sub lattice and B has restored its sub lattice and of course B has switched its position. There is still 1 antisite left that is A' on B. The last jump of the vacancy will be with this antisite A' on B. A prime has also restored its sub lattice now. But you can see after six jumps, A and A' has swapped their positions.

The vacancy has also swapped its position with B along the 110 direction position. After the sequence of six jumps of this vacancy, two A atoms which were next nearest neighbours of each other have swapped their position and vacancy on B sub lattice has swapped its position with a B atom along 110 direction and at the end of sixth jump the order is restored. No wrong bonds are left, so this is one unit step of diffusion and this is called as SJVC, sixth jump vacancy cycle.

At the end of this particular SJVC, the vacancy has moved along 110 and this is denoted as [110] SJVC. We can also have a sequence of jumps of this vacancy such that the vacancy will move along 100 at the end of six jumps and that will be [100] SJVC. Now again within that [100] SJVC there are two variants, either all jumps may be in the same plane, which is denoted as straight [100] SJVC or some jumps may be out of plane which is denoted as bent [100] SJVC.

That you can do as exercise to create a sequence of six jumps of straight [100] SJVS and bent [100] SJVC. This mechanism is quite active in B_2 type of crystal structures, in particularly in NiAl many researchers have shown the energy barrier for SJVC may be much less than energy barrier for NNNJ or next nearest neighbour jumps.

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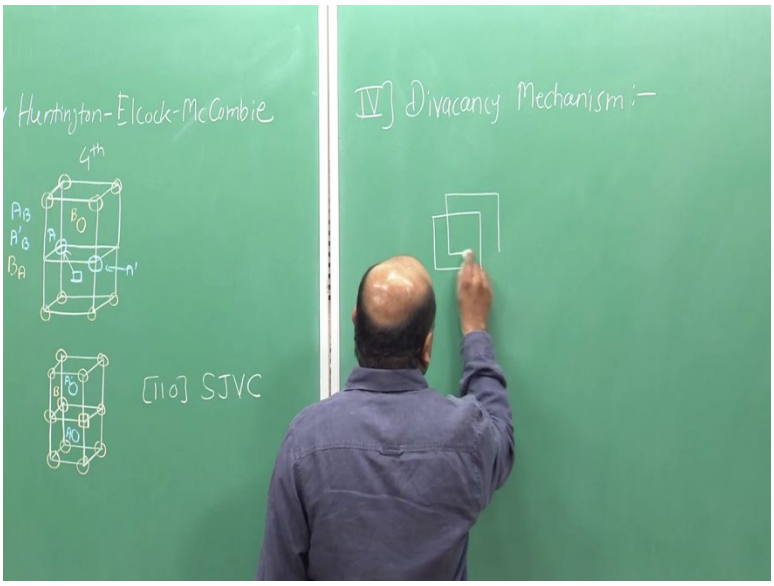

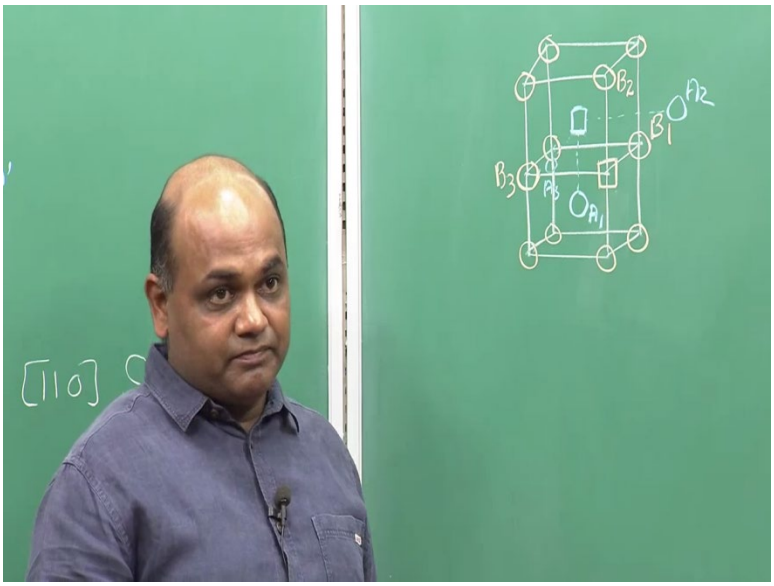

One more mechanism that we are going to look at is Divacancy mechanism. Divacancy is a pair of vacancies on two nearest neighbour sites. Obviously one vacancy is on A sub lattice, the other is on B sub lattice in a B_2 structure. This is a schematic of B_2 crystal which shows a divacancy.

You can see there is one vacancy on A sub lattice and there is another vacancy which is the nearest neighbour of this vacancy and it is on B sub lattice. In a divacancy mechanism, the divacancy moves as a pair which means during the diffusion, the divacancy never disassociates. For this to occur all jumps are TripleJ, next nearest neighbour jumps. Now if all jumps have to take place by next nearest neighbour jump and the divacancy should never dissociate, any individual vacancy will be able to jump on to 3 next nearest neighbour sites. We know in B_2

there are 6 next nearest neighbour site to any atom. But we have to select the sites which are next nearest neighbour to the first vacancy, at the same time those sites have to be nearest neighbour of the second vacancy. There are 3 such sites. if we consider this particular vacancy on B. We can denote the 3 sites as B_1, B_2 and B_3. The first one is B_1, which is also a nearest neighbour of the vacancy on A, the second one is B_2 which is next nearest neighbour for vacancy on B but nearest neighbour for vacancy on A and B_3 this is also nearest neighbour of vacancy on A.

Similarly, there are 3 sites on which the vacancy on A can jump by NNNJ individually and these 3 sites are also nearest neighbour of the vacancy on B. First one is obviously the A atom, which is shown in the cube under the first one here. Second A atom would be in the cube on the right side and third A atom would be in the cube which is placed in front of this top cube here, this is A_3. These are the three atoms onto which the vacancy on A can jump individually. So, this is divacancy mechanism.

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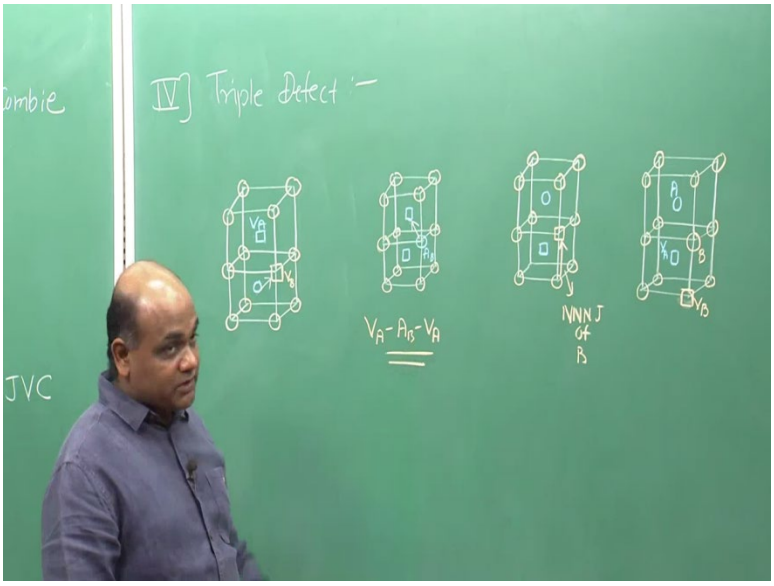

The last mechanism that we are going to look at is triple defect mechanism. In the last class, we have seen triple defect is a defect complex which consists of 2 vacancies and 1 antisite. In the tripe defect mechanism the diffusion is assisted by the formation of a triple defect. So, this is a schematic B_2 structure, I have shown 2 unit cubes which with a divacancy or a pair of vacancies on nearest neighbor site.

One on A sub lattice this is V_A, the other one on B sub lattice this is V_B. Now if A atom happens to be small, it can jump onto the nearest neighbor vacancy on B and it will lead to formation of an antisite and the vacancy will move to A sub lattice. So, A will form an antisite A_B. Now we can see, it has formed a triple defect which involves 2 vacancies on A sub lattice and one A_B antisite. This is a triple defect: V_A, A_B and V_B. That is why this is called as triple defect.

On its next jump the antisite A can exchange with the other vacancy by nearest neighbor jump. A will restore its position in A sub lattice. But it has changed its site obviously on the A sub lattice, the vacancy has moved to B sub lattice and B atom being larger, can diffuse by tripleJ or next nearest neighbor jumps. Now this B atom can jump into this vacant site, this is NNNJ of B. B has now moved here, this is A, this is B, vacancy on A and vacancy on B.

So if we compare with where we started, the divacancy V_A and V_B has in effect moved to next nearest neighbor site. Also one A atom and one B atom have moved to next nearest neighbor site. This is how the triple defect assists the diffusion process in B_2 intermetallic. These are some of the important diffusion mechanisms that have been proposed in intermetallics and I have illustrated it with respect to B_2 sub lattice. I will stop here for today, thank you.